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㊹発明の名称　繊維製品の消臭加工方法

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明　細　書

1．発明の名称

繊維製品の消臭加工方法

2．特許請求の範囲

フラボン系化合物、テルペン系化合物又はポルフィリン金属錯体化合物を有効成分とする消臭組成物と、セルロース反応型撥水剤及び樹脂加工剤との混合液を天然繊維又は再生繊維の単独或は天然繊維又は再生繊維と合成繊維との複合物からなる繊維製品に付与し熱処理することを特徴とする洗濯耐久性の有る消臭加工繊維製品の製造方法。

3．発明の詳細な説明

【技術分野】

本発明は新規な消臭繊維製品の製造方法に関し、更に詳しくは、植物の消臭性抽出物を有効成分とする消臭組成物と、セルロース反応型撥水剤と樹脂加工剤との混合液で繊維製品（糸、編物、織物、不織布など）を処理して洗濯耐久性の優れた消臭作用を有する繊維製品を製造する方法に関するものである。

【従来技術】

植物成分中に消臭作用を有する物質が存在することはよく知られておりその中には既に消臭剤として実用化されているものも幾つかある。

例えば、特開昭50−160434号公報にはクロロフィルとセルドレン系化合物含有精油とを含有するゴム悪臭含有ガス用消臭組成物が開示されており、また、特開昭58−61751号公報及び特開昭59−66号公報にはシソ科植物の或る種の抽出物が硫黄化合物に対し消臭効果を示すことが記載されている。

これらの植物からの抽出物の消臭効果のメカニズムは明らかではないが、クロロフィルのようなポリフィリン金属錯体系化合物により酸化還元作用、或いはフラバノール、フラボノール類の如きフラボン系化合物又はフエラドレン、ターピネン、ピネン等のテルペン系化合物及びその他多数の有機高分子類による包接作用、付加作用、中和反応等の複合作用によって消臭効果が生ずるものと推定されている。

これらの植物からの抽出物を有効成分とする消臭剤は、化学薬品のような薬害や環境汚染等の問題が少なく、シャンプー、ヘアトニック、石鹸、練歯磨、マウスウオッシュなどへの添加、室内やトイレの消臭用、工　排気の脱臭、フイルター型空気清浄器用、消臭壁紙、食品、例えばチューインガム、キャンデイへの配合等多くの用途に使用されている。

しかし、これら植物から抽出した消臭剤成分は水に可溶性のものが多く、消臭剤成分単独で繊維に加工したものは洗濯等で消臭有効成分が溶け出して効果が持続しないという欠点がある。

［目　的］

本発明者らは、植物から抽出した消臭成分を有効成分とする消臭剤における上記欠点を解消すべく鋭意検討を行なった結果、該消臭剤とセルロース反応型撥水剤及び樹脂加工剤並びに場合によりさらに触媒とを併用後熱処理することにより加工した繊維の消臭効果が繰り返し洗濯後も持続する加工方法を見い出し本発明を完成するに至った。

［発明の構成］

本発明によれば、フラボン系化合物又はテルペン系化合物或はポルフイリン金属錯体系化合物の一種又は複合物を消臭剤として、セルロース反応型撥水剤と樹脂加工剤とを配合した混合物で繊維製品を処理することを特徴とする洗濯耐久性に優れた消臭繊維製品が提供される。

該混合物により加工した繊維製品の消臭効果が繰返し洗濯後も持続するメカニズムは明らかではないが、セルロース反応型撥水剤と樹脂加工剤との相乗作用により消臭成分が繊維に強固に固着されるためと推定される。

本発明の特徴は植物中に存在する消臭効果のある成分とセルロース反応型撥水剤及び樹脂加工剤とを併用する点にある。

しかして、本発明の消臭組成物において有効成分として使用される植物中に存在する消臭効果のある成分（以下「消臭成分」という）としては次のものが挙げられる。

(a)　フラボン系化合物：フラボン類（例：フラボン）、フラボノール類（例：ルチン）、イソフラボン類（例：ゲニステイン、ダイゼイン）、フラバノン類（例：ヘスペンチン）、フラバノール類（例：フスチン、アルピノン）など又はこれらの2種以上の混合物。

(b)　テルペン系化合物：例えばピネン、テルピネン、フエランドレン、カンフエン、リモネン、カジネン、ビダポレン、カンホレンなど又はこれら2種以上の混合物。

(c)　ポルフイリン金属錯体化合物：例えば、クロロフイル、クロロフイリンナトリウム塩など。

これらの化合物は純品であってもよいが、通常、植物からの抽出エキスの状態のもので充分である。また、これらの化合物は単独で用いてもよく、或いは、2種類以上組合わせて使用することもできる。

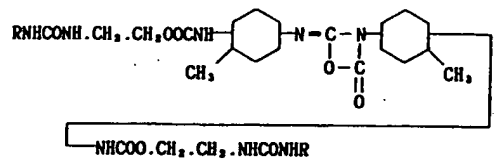
例えば、フラボン系化合物を多く含むものとして、特開昭58－61751号に記載されているツバキ科植物、例えば茶、山茶花、椿、サカキ、ヒサカキ等の主として葉部からの水、アルコール系溶媒、ケトン系溶媒による抽出物。

或いはこれら植物の乾留液が挙げられ、またテルペン系化合物を多く含むものとして、既に知られている針葉樹、例えばアカマツ、スギ、ローソン、ヒノ木、チヤボヒバ等の乾留液が好適である。

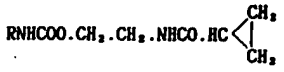
併用するセルロース反応型撥水剤としては、弗素系又はシリコン系或いはアルキルエチレン尿素系のものが挙げられる。

弗素系撥水剤としては、パーフルオロアルキル酸エステルを主成分とする共重合体が挙げられ、シリコン系撥水剤としてはメチルハイドロジエンシロキサン等が包含される。

アルキルエチレン尿素系撥水剤としては、イソシアネートのダイマー、モノエタノールアミン、高級アルキルイソシアネートより合成された下記式



の化合物と、シクロプロパンモノカルボン酸、モノエタノールアミン、高級アルキルイソシアネートから合成された下記式



の化合物

（商品名：パラジウム、大原パラジウム化学製）の配合品があげられる。

これら撥水剤の配合量は厳密に制限されるものではなく広範にわたって変えることが出来るが、撥水剤は一般には消臭成分1重量部当り1～10重量部の範囲内で使用するのが適当である。

また使用する樹脂剤としてはグリオキザル系樹脂、エチレン尿素樹脂、メラミン樹脂、尿素樹脂、エポキシ樹脂、アクリル酸エステル系樹脂等が挙げられる。

これら樹脂剤の配合率は消臭成分の種類や本発明の消臭加工繊維製品の使用目的等に応じて広範にわたり適宜変えることが出来るが、樹脂剤は、一般に消臭成分1重量部に対して5～20重量部の範囲で使用するのが好ましい。

更に、樹脂加工剤の反応促進剤としてホウ弗化亜鉛、有機アミン塩、金属塩、或いは、硝酸亜鉛等の単独又は混合触媒が使用出来る。

触媒の使用量は樹脂加工剤100重量部に対して10～30重量部の範囲が好ましい。

使用し得る液体媒体としては水或いは水に少量のアルコール（例：エタノール）が混合されたものが挙げられる。

またこれら液体媒体への消臭成分の溶解性を高めるために、液体媒体には界面活性剤殊に非イオン界面活性剤を配合することが出来る。

さらに、繊維製品として望まれる特性を付与するため柔軟剤、例えば脂肪酸エステル高級アルコール硫酸化物等を適宜配合してもよい。

繊維としては、綿、麻等の天然繊維或いはビスコースレーヨン、キュプラ等の再生繊維系繊維の単独、又はこれら天然繊維或いは再成繊維と合成繊維、例えばポリエステル、ナイロン、ポリアクリルニトリル繊維等との混紡品であっても交織物でもよい。

本発明の方法では消臭成分をセルロース反応型撥水剤及び樹脂剤との混合物と共に繊維に付着させた後、熱処理して固着させる。

混合物は例えば、消臭組成物（フラボン系、テルペン系、クロロフィル含有物）0.5～15gを水500mlに希釈し必要に応じてドデシルベンゼンスルフォン酸ソーダ、ポリエチレングリコールソルビタンモノステアレートの如き非イオン系界面活性剤0.1～2gを添加し、更にアルキルエチレン尿素系のセルロース反応型撥水剤5～20g及びグリオキザル系樹脂剤10～15gと触媒ホウ弗化亜鉛0.1～3.0gを添加して調製することが出来る。

この混合液に繊維を浸漬後所定含有する様に絞り次いで乾燥、加熱処理する。乾燥は通常80～120℃で4～5分程度とすることができ、また、加熱処理は130～165℃で1～5分間とすることができる。加熱処理後は必要に応じて水洗を行なう。

以上述べた本発明の消臭効果を有する繊維品の加工方法は、後記実施例から明らかなように、消臭成分のみ消臭成分と撥水剤の組合わせ又は消臭成分と樹脂加工剤の組合せを使用した成分と比べて繰返し洗濯後の消臭効果の持続性がはるかに優れている。

[実施例]

次に実施例を挙げて本発明をさらに具体的に説明する。

なお、実施例におけるアンモニア又は硫化水素の消臭率は次の様にして求めたものである。

試料溶液に精練、漂白した布を浸漬後、マングルで搾液して絞り率100%で乾燥した。

この処理した布又は処理後洗濯した布10gを予め用意した所定濃度のアンモニアガス又は硫化水素ガスの入った内容1000mlガラス瓶に入れ

密栓し、1時間放置後のアンモニアガス又は硫化水素ガス濃度を北川式検知管で測定してアンモニアガス又は硫化水素ガスに対して下記式により消臭率を求める。

$$消臭率(\%)=\left(1-\frac{測定時NH_3又はH_2S濃度}{初期NH_3又はH_2S濃度}\right)\times 100$$

また、実施例における洗濯は浴比1：20、洗剤1g／ℓを用い40℃の温水で3分間洗浄、脱水、流水で10分間すすいだ後、脱水、乾燥の操作を一回とした。

実施例　1

針葉樹精から抽出したテルペン系化合物を含有する消臭剤（ココノエ製；スーパークリーンKS－YM）5gとセルロース反応型撥水剤（明成化学製；パラジットRSN）15gとメラミン系樹脂（住友化学製；スミテックスレジンM－3）30g及びホウフッ化亜鉛4gを水500mℓに溶解して混合液を調製した。

上記の混合液に精練、漂白した綿布を浸漬後、マングルを用いて100%に絞り、80℃で5分間乾燥した。

次に140℃で3分間熱処理を行なって、充分樹脂を固着した後、水洗を行なって、消臭加工布（A）を得た。

比較の為、上記消臭剤（スーパークリーンKS－YM）5gを水500mℓで希釈した液で綿布を処理乾燥して比較布（B）を得た。

こうして得られた消臭加工綿布（A）及び（B）の洗濯前と洗濯後の消臭率は次の通りであった。

第1表　アンモニア消臭率（アンモニア濃度；150ppm）

消臭加工布	消臭率（%）		
	洗濯前	洗濯10回	洗濯30回
A（本発明）	80	65	45
B（比較例）	80	0	0
ブランク	0	0	0

註：洗剤はモノゲン(第一工業製薬)を使用した。

実施例　2

鉄クロロフィル1gを非イオン界面活性剤（ドデシルベンゼンスルフオン酸ソーダ）0.5gと均一に混合後、水500mℓに溶解した。

その水溶液にセルロース反応型フッソ系撥水剤（明成化学製ペトロックス3000）15gとグリオキザール系樹脂（住友化学製スミテックスレジンFSK）30g及び塩化マグネシウムを主成分とする金属塩系触媒（大日本インキ製カタリストM）6gとを混合して液を調製した。上記混合液に精練漂白した綿布を浸漬後、マングルを用いて100%に絞り80℃で5分間乾燥した。

次に140℃で3分間熱処理後、水洗を行ない消臭加工布（C）を得た。

比較の為、鉄クロロフィル1gと非イオン界面活性剤0.5gを均一に混合後、水500mℓに溶解させた水溶液で綿布を処理して比較布（D）を得た。

上記消臭加工布（C）及び（D）の消臭率は次の通りであった。

第2表　硫化水素消臭率（硫化水素濃度；80ppm）

消臭加工布	消臭率（%）		
	洗濯前	洗濯10回	洗濯30回
C（本発明）	80	45	35
D（比較例）	80	10	0
ブランク	0	0	0

註：洗剤はニユービーズ(花王)を使用した。

実施例　3

茶樹から抽出したフラボン系化合物を含有する消臭剤（白井松新薬製フレッシュシライマツ）12.5gとセルロース反応型撥水剤（大原パラジウム製パラジウムRC）15gとメラミン系樹脂（住友化学製スミテックスレジンM－3）30gと有機アミン塩系触媒（大日本インキ製カタリスト376）4gを水500mℓに溶解して混合液を調製した。

上記混合液に精練、漂白した綿布を浸漬後、マングルを用いて100%に絞り80℃で5分間乾燥した。

次に１４０℃で３分間熱処理後、水洗を行ない消臭加工布（Ｅ）を得た。

比較の為、撥水剤のみ併用した場合の例として消臭剤（白井松新薬製フレッシュシライマツ）１２.５gとセルロース反応型撥水剤（大原パラジウム製パラジウムＲＣ）１５gを水５００mℓに溶解して混合液を調製した。

上記混合液に綿布を浸漬後、マングルを用いて絞り乾燥した。

次に１４０℃で３分間熱処理後、水洗を行ない比較布（Ｆ）を得た。

更に比較の為、樹脂のみを併用した例として消臭剤（白井松新薬製フレッシュシライマツ）１２.５gとメラミン系樹脂（住友化学製スミテックスレジンＭ－３）３０gと有機アミン塩系触媒（大日本インキ製カタリスト３７６）４gを水５００mℓに溶解して混合液を調製した。

上記混合液に綿布を浸漬後、マングルを用いて１００％に絞り乾燥した。

次に１４０℃で３分間熱処理後水洗を行ない比較布（Ｇ）を得た。

こうして得られた消臭加工布（Ｅ）及び（Ｆ）、（Ｇ）の洗濯前と洗濯後の消臭率は次の通りであった。

第３表　硫化水素消臭率（硫化水素濃度：８０ppm）

消臭加工布	消臭率（％）		
	洗濯前	洗濯10回	洗濯30回
Ｅ（本発明）	75	45	40
Ｆ（比較例）	75	0	0
Ｇ（　〃　）	0	0	0
ブランク	0	0	0

註：洗剤はモノゲン(第１工業製薬)を使用した。

実施例　４

フラボン系化合物を含有する消臭剤（リリース科学製；パンシル）５gとセルロース反応型撥水剤（大原パテジウム製パラジウムＡＶ）１５gとメラミン系樹脂（住友化学製スミテックスレジンＭ－１０）３０gとホウフッ化亜鉛４gを水５００mℓで希釈して混合液を調製した。

上記混合液にポリエステル／綿混紡布を浸漬後、マングルを用いて８０％に絞り乾燥した。

次に１４０℃で３分間熱処理後、水洗を行ない消臭加工布（Ｇ）を得た。

比較のため消臭剤パンシル２.５gを水５００mℓで希釈した液で、ポリエステル／綿混紡布を処理して比較布（Ｈ）を得た。

得られた消臭加工布（Ｇ）及び（Ｈ）の消臭率は次の通りであった。

第４表　アンモニア消臭率（アンモニア濃度：２００ppm）

消臭加工布	消臭率（％）		
	洗濯前	洗濯10回	洗濯30回
Ｇ（本発明）	80	50	45
Ｈ（比較例）	80	0	0
ブランク	0	0	0

註：洗剤はニューピーズ(花王)を使用した。

実施例　５

フラボン系化合　を含有する消臭剤（大和化学製アステンチＰ－１１０）５gとセルロース反応型撥水剤（大原パラジウム製パラジウムＲＣ）１５gとメラミン系樹脂（住友化学製スミテックスレジンＭ－３）３０gと金属塩系触媒（大日本インキ製カタリストＭ）及び有機アミン塩系触媒(大日本インキ製カタリスト３７６）２gを水５００mℓに溶解して混合液を調製した。

上記混合液に綿布を浸漬後、マングルを用いて１００％に絞り乾燥した。

次に１４０℃で３分間熱処理後水洗を行ない消臭加工布（Ｉ）を得た。

比較のため、上記消臭剤アステンチＰ－１１０５gを水５００mℓで希釈した液で綿布を処理して比較布（Ｊ）を得た。

得られた消臭加工布（Ｉ）及び（Ｊ）の消臭率は次の通りであった。

第５表　アンモニア消臭率（アンモニア濃度：１５０ppm）

消臭加工布	消臭率（％）		
	洗濯前	洗濯10回	洗濯30回
Ｉ（本発明）	80	55	45
Ｊ（比較例）	80	0	0
ブランク	0	0	0

註：洗剤はモノゲン(第一工業製薬)を使用した。

実施例　6

ツバキ科植物から抽出したフラボン系化合物を含有する消臭剤（白井松新薬製）５gと、セルロース反応型撥水剤（大原パラジウム製パラジウムＲＣ）１５gとエポキシ系樹脂（長瀬産業デナコールＥＸ８１０）３０gを水５００mlに溶解して混合液を調製した。

上記混合液に精練、漂白した綿布を浸漬後、マングルを用いて１００％に絞り８０℃で５分間乾燥した。

次に１４０℃で３分間熱処理後水洗を行ない消臭加工布（Ｋ）を得た。

の用途は衣料、寝装品等広範に及ぶものである。

特許出願人　日清紡績株式会社
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同　　弁理士　江　角　洋　治

比較のため、上記消臭剤５gを水５００mlで希釈した液で綿布を処理して比較布（Ｌ）を得た。

得られた消臭加工布（Ｋ）及び（Ｌ）の消臭率は次の通りであった。

第６表　硫化水素消臭率（硫化水素濃度：８０ppm）

消臭加工布	消臭率（％）		
	洗濯前	洗濯10回	洗濯30回
Ｋ（本発明）	75	50	40
Ｌ（比較例）	75	0	0
ブランク	0	0	0

註：洗剤はモノゲン(第一工業製薬)を使用した。

［結　果］

以上、詳述したように、フラボン系化合物、テルペン系化合物又はポルフィリン金属錯体化合物を有効成分とする消臭組成物とセルロース反応型撥水剤及び樹脂剤との混合液で繊維製品を加工する方法は現行の繊維製品の樹脂加工装置で容易に行なうことが出来る。

また、製品の洗濯耐久性が優れているので、そ

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Japanese Patent

Document No. 1-213484

METHOD FOR DEODORIZING A FIBER PRODUCT

[Sen'i Seihin no Shoshu Kako Hoho]

Kiyoshi Ito and Yoshifumi Matsuda

UNITED STATES PATENT AND TRADEMARK OFFICE

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/1[1]

Specification

1. Title of the invention

Method for deodorizing a fiber product

2. Patent Claim

A method for manufacturing a deodorized fiber product endowed with a wash resistance characterized by the fact that a liquid mixture of a deodorizing composition which includes, as an effective component, a flavonic compound, a terpenic compound, or a porphyrin-metal complex compound together with a cellulose-reactive water repellent agent and a resin processing agent is applied to a fiber product which consists either of a natural fiber or regenerated fiber alone or a composite of a natural fiber or regenerated fiber and a synthetic fiber and that the obtained product is thermally treated.

3. Detailed explanation of the invention

(Technical fields)

The present invention concerns a novel method for manufacturing a deodorized fiber product, and more specifically, it concerns a method for manufacturing a fiber product which exhibits an excellent wash resistance and which serves a deodorizing function by treating a fiber product (e.g., yarns,

[1] Numbers in the margin indicate pagination in the foreign text.

knitted fabrics, woven fabrics, non-woven fabrics, etc.) with a liquid mixture of a deodorizing composition which includes a deodorizing plant extract as an effective component together with a cellulose-reactive water repellent agent and a resin processing agent.

(Prior art)

It is well-known that substances which serve deodorizing functions exist among plant components, and some of them have already been provided as practical deodorizers.

A deodorizing composition for a gas with a rubbery odor which includes chlorophyll and a serdolenic compound-containing essential oil, for example, is mentioned in Japanese Patent Application Publication No. Kokai Sho 50[1975]-160434 Gazette, whereas it is mentioned in Japanese Patent Application Publication No. Kokai Sho 58[1983]-61751 Gazette and Japanese Patent Application Publication No. Kokai Sho 59[1984]-66 that the extracts of certain types of Lamiaceae plants exert deodorizing effects on sulfur-containing compounds.

The mechanisms of the deodorizing effects ascribed to the extracts of these plants have yet to be clarified, although such deodorizing effects are presumed to arise from either oxidation/reduction functions ascribed to porphyrin-metal complex compounds (e.g., chlorophyll, etc.) or composite functions (e.g., inclusion function, addition function, neutralizing reaction, etc.) ascribed to flavonic compounds (e.g., flavanol, flavonol,

etc.) or terpenic compounds (e.g., phellandrene, terpinene, pinene, etc.).

Deodorizers which include, as effective components, the extracts obtained from these /2
plants are virtually unaccompanied by toxicity hazards or environmental pollutions, etc. unique to chemical drugs, and accordingly, they are being used for diverse purposes (e.g., additives for shampoos, hair tonics, soaps, toothpastes, mouth washes, etc., indoor or bathroom odor masking, deodorization of industrial exhaust gases, air cleaning filter applications, deodorizing wall papers, ingredients of foods such as chewing gums, candies, etc., etc.).

Many of the deodorizer components extracted from these plants, however, are soluble with water, and in a case where such a deodorizing component is used alone for treating a fiber, the deodorizing effective component becomes eluted as a result of washing, etc., which is problematic in that the lasting effect cannot be expected.

(Objective)

The present inventors compiled exhaustive research in order to eradicate the aforementioned shortcomings associated with deodorizers which include, as effective components, deodorizing components extracted from plants, as a result of which the present invention has been completed after it had been discovered that a treatment method which is capable of perpetuating the deodorizing

effect of a treated fiber even after repeated wash cycles can be provided by using said deodorizer with a cellulose-reactive water repellent agent and a resin processing agent as well as, if necessary, a catalyst and by subsequently performing a thermal treatment.

(Constitution of the invention)

The present invention provides a deodorized fiber product endowed with an excellent wash resistance characterized by the treatment of a fiber product with a mixture obtained by mixing a deodorizer constituted either by a singular type of a flavonic compound, a terpenic compound, or a porphyrin-metal complex compound or by their composite with a cellulose-reactive water repellent agent and a resin processing agent.

The mechanism by which the deodorizing effect of the fiber product treated with said mixture is perpetuated even after repeated wash cycles has yet to be clarified, although the deodorizing component is presumed to become firmly fixed and adhered to the fiber as a result of the synergistic effects of the cellulose-reactive water repellent agent and resin processing agent.

The present invention is peculiarly characterized by the combined uses of a component which exists within a plant and which exerts a deodorizing effect with a cellulose-reactive water repellent agent and a resin processing agent.

The following concretely instantiate such components which exist within plants and which exert deodorizing effects, namely the effective component of the deodorizing composition of the present invention (hereafter referred to as the "deodorizing components"):

(a): Flavonic compounds: Flavones (e.g., flavone, etc.), flavonols (e.g., rutin, etc.), isoflavones (e.g., genistin, daizein, etc.), flavanones (e.g., hespentin [sic: Presumably "hesperetin"], etc.), flavanols (e.g., fustin, albinol, etc.), and/or mixtures of two or more types of these examples;

(b): Terpenic compounds: Namely, pinene, terpinene, phellandrene, camphene, limonene, cadinene, pidaborene, camphorene, and/or mixtures of two or more types of these examples;

(c): Porphyrin-metal complex compounds: Namely, chlorophyll, chlorophyllin sodium salt, etc.

These compounds may be pure products, although ones characterized by plant extract states normally suffice. These compounds may, furthermore, be used alone or in combination of two or more types.

Ones which include abundant flavonic compounds may, for example, be instantiated by extracts of Theaceae plants (e.g., tea, sasanqua, camellia, sakaki, hisakaki, etc.) mentioned in Japanese Patent Application Publication No. Kokai Sho 58[1983]-61751, especially extracts of their leaves obtained by using water, alcoholic solvents, and/or ketonic solvents

Or dry distillates of these plants, whereas ones which include abundant terpenic compounds are favorably instantiated by dry distillates of traditionally known conifers (e.g., Japanese red pine, cryptomeria, Lawson [sic: presumably "lauan"], hinoki, chabo cedar, etc.).

Ones of the fluorine, silicone, and/or alkylethyleneurea types are conceivable as the concomitantly used cellulose-reactive water repellent agent.

Fluorine-type water repellent agents are instantiated by copolymers which include perfluoroalkyl acid esters as main components, whereas silicone-type water repellent agents are instantiated by methylhydrodiene-siloxane, etc.

Alkylethyleneurea-type water repellent agents are instantiated by a mixture of a compound represented by the following formula:

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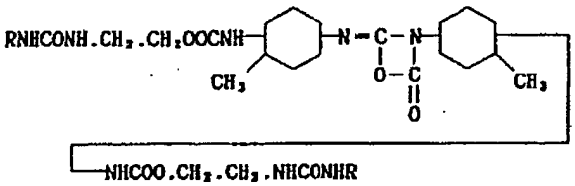
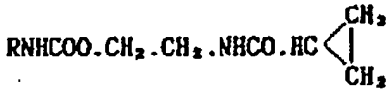


which is synthesized from the dimer of an isocyanate, monoethanolamine, and a low-molecular-weight alkyl isocyanate, and a compound represented by the following formula:



which is synthesized from cyclopropanemonocarboxylic acid, monoethanolamine, and a high-molecular-weight alkyl isocyanate (trademark: "Palladium," manufactured by Ohara Palladium Chemical Co.).

There are no strict restrictions on the mixing ratios of these water repellent agents, and accordingly, they may be varied over a broad spectrum, although it is generally desirable for the utilization ratio of the water repellent agent with respect to 1 part by weight of the deodorizing component to be confined to a range of 1 ~ 10 parts by weight.

Concomitantly used resin processing agents, furthermore, are instantiated by glyoxalic resins, ethyleneurea resins, melamine resins, urea resins, epoxy resins, acrylic acid ester resins, etc.

The mixing ratios of these resin processing agents may be varied over a broad spectrum depending on the types of deodorizing components or on the application objectives of the deodorized fiber product of the present invention, although it is generally desirable for the utilization ratio of the resin processing agent with respect to 1 part by weight of the deodorizing component to be confined to a range of 5 ~ 20 parts by weight.

Catalysts constituted either by zinc borofluoride, organic amine salts, metal salts, zinc borate, etc. alone or by their mixtures may, furthermore, be employed as reaction accelerators for the resin processing agents.

It is desirable for the utilization ratio of the catalyst with respect to 100 parts by weight of the resin processing agent to be designated within a range of 10 ~ 30 parts by weight.

Either water or a mixture obtained by mixing a small quantity of an alcohol (e.g., ethanol, etc.) with water is conceivable as a concomitantly usable liquid medium.

It is also possible to mix surfactants, especially nonionic surfactants, with these liquid media for the purpose of elevating the solubilities of the deodorizing components with these liquid media.

It is also possible, furthermore, to mix softening agents (e.g., fatty acid ester high-molecular-weight alcohol sulfated products, etc.) adventitiously for the purpose of conferring desirable attributes on the fiber product.

Natural fibers (e.g., cotton, hemp, etc.) or regenerated fibers (e.g., viscose rayon, cupra, etc.) alone may be used as fibers, or mix-spun or woven fabrics of these natural fibers or regenerated fibers and synthetic fibers (e.g., polyester, nylon, polyacrylonitrile, etc.) may be used instead.

As far as the method of the present invention is concerned, a mixture of the deodorizing component, cellulose-reactive water repellent agent, and resin processing agent is adhered to a fiber and then fixed and bound by means of a thermal treatment.

Said mixture may, for example, be prepared by diluting 0.5 ~ 15 g of a deodorizing composition (e.g., flavonic type, terpenic type, crude chlorophyll, etc.) with 500 mL of water, by then

adding, if necessary, a nonionic surfactant (e.g., sodium dodecylbenzenesulfonate, polyethylene glycol sorbitan monostearate, etc.) to the obtained mixture, and by eventually adding 5 ~ 20 g of an alkylethyleneurea-type cellulose-reactive water repellent agent, 10 ~ 15 g of a glyoxalic resin processing agent, and 0.1 ~ 3.0 g of a zinc borofluoride catalyst to the obtained mixture.

After the fiber has been immersed into the obtained liquid mixture, it is wrung for optimizing the liquid internalization ratio, dried, and then thermally treated. The drying treatment is normally performed at 80 ~ 120°C for approximately 4 ~ 5 min., whereas the thermal treatment is performed at 130 ~ 165°C for 1 ~ 5 min. The thermally treated product may, if necessary, be washed with water.

As the application examples shown below clearly suggest, as far as the aforementioned method of the present invention for processing a fiber product endowed with a deodorizing effect is concerned, the lasting deodorizing effect after repeated wash cycles is far superior to that of a case where the deodorizing component alone is used, where the deodorizing component and water repellent agent are used in combination, or where the deodorizing component and resin processing agent are used in combination.

(Application examples)

Next, the present invention will be explained more concretely with reference to application examples.

Incidentally, the ammonia or hydrogen sulfide deodorizing efficiency in the application examples was calculated according to the following procedures.

After a scoured and bleached fabric had been immersed in a sample solution, the liquid was wrung out by using a mangle and then dried at a wring ratio of 100%.

10 g of the fabric thus treated or a fabric which had been likewise treated and then washed was filled and sealed into a preliminarily prepared glass bottle (content volume: 1,000 mL) into which gaseous ammonia or gaseous hydrogen sulfide had been charged at a certain concentration, and after the system had been left unattended for 1 hour, the gaseous ammonia or gaseous

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hydrogen sulfide concentration was measured by using a Kitagawa detection tube, and the gaseous ammonia or gaseous hydrogen sulfide deodorizing efficiency was calculated by using the following formula:

Deodorizing efficiency (%) = (1 - NH_3 or N_2S concentration at the time of measurement/initial NH_3 or N_2S concentration) x 100.

Moreover, a washing operation wherein a 3-min. washing phase in a 40°C hot water system (bath ratio: 1 : 20; detergent: 1 g/L) is followed by a dehydration phase, a 10-min. flowing water rinsing phase, another dehydration phase, and then a drying phase was defined as a single cycle in the application examples.

Application Example 1

A liquid mixture was prepared by solubilizing 5 g of a deodorizer which had been extracted from a conifer tree and which included a terpenic compound ("Super Clean KS-YM," manufactured by Kokonoe Co.), 15 g of a cellulose-reactive water repellent agent ("Parasit RSN," manufactured by Meisei Chemical Co.), 30 g of a melamine resin ("Sumitex Resin M-3," manufactured by Sumitomo Chemical Co.), and 4 g of zinc borofluoride into 500 mL of water.

After a scoured and bleached cotton fabric had been immersed into the aforementioned liquid mixture, it was wrung at 100% by using a mangle and then dried at 80°C over a 5-min. period.

Next, it was thermally treated at 146°C over a 3-min. period, as a result of which the resin became sufficiently fixed and bound, and after it had been washed with water, the deodorizing fabric (A) was obtained.

For comparative purposes, a cotton fabric was treated with a solution obtained by diluting 5 g of the aforementioned deodorizer ("Super Clean KS-YM") with 500 mL of water, as a result of which the comparative fabric (B) was obtained.

The respective deodorizing efficiencies of the deodorizing fabric (A) and (B) thus obtained before and after the wash cycles are shown below.

Table I: Ammonia deodorizing efficiency

(ammonia concentration: 150 ppm)

Deodorizing fabric	Deodorizing efficiency (%)		
	Pre-wash	10 wash cycles	30 wash cycles
A (Present invention)	80	65	45
B (comparative example)	80	0	0
Blank	0	0	0

[Note: "Monogen" (manufactured by Daiichi Seiyaku Co.) was used as a detergent]

Application Example 2

After 1 g of iron-chlorophyll and 0.5 g of a nonionic surfactant (sodium dodecylbenzenesulfonate) had been homogeneous mixed with one another, the obtained mixture was solubilized into 500 mL of water.

15 g of a cellulose-reactive water repellent agent ("Betrox 3000," manufactured by Meisei Chemical Co.), 30 g of a glyoxalic resin ("Sumitex Resin FSK," manufactured by Sumitomo Chemical Co.), and 5 g of a metal salt-type catalyst which included magnesium chloride as a main component ("Catalyst M," manufactured by Dai-Nihon Ink Chemical Co.) were mixed with the obtained aqueous solution, as a result of which a liquid mixture was

obtained. After a scoured and bleached cotton fabric had been immersed into the aforementioned liquid mixture, it was wrung at 100% by using a mangle and then dried at 80°C over a 5-min. period.

Next, it was thermally treated at 140°C over a 3-min. period, and after it had been washed with water, the deodorizing fabric (C) was obtained.

For comparative purposes, a cotton fabric was treated with an aqueous solution obtained by homogeneously mixing 1 g of iron-chlorophyll and 0.5 g of said nonionic surfactant and by solubilizing the obtained mixture into 500 mL of water, as a result of which the comparative fabric (D) was obtained.

The respective deodorizing efficiencies of the deodorizing fabric (C) and (D) thus obtained before and after the wash cycles are shown below.

Table II: Hydrogen sulfide deodorizing efficiency

(hydrogen sulfide concentration: 80 ppm)

Deodorizing fabric	Deodorizing efficiency (%)		
	Pre-wash	10 wash cycles	30 wash cycles
C (Present invention)	80	45	35
D (comparative example)	80	10	0
Blank	0	0	0

[Note: "New Beads" (manufactured by Kao Co.) was used as a detergent]

Application Example 3

A liquid mixture was prepared by solubilizing 12.5 g of a deodorizer which had been extracted from a tea tree and which included a flavonic compound ("Fresh Shiraimatsu," manufactured by Shiraimatsu Shin'yaku Co.), 15 g of a cellulose-reactive water repellent agent ("Palladium," manufactured by Ohara Palladium Chemical Co.), 30 g of a melamine resin ("Sumitex Resin M-3," manufactured by Sumitomo Chemical Co.), and 4 g of an organic amine salt-type catalyst ("Catalyst 376," manufactured by Dai-Nihon Ink Chemical Co.) into 500 mL of water.

After a scoured and bleached cotton fabric had been immersed into the aforementioned liquid mixture, it was wrung at 100% by using a mangle and then dried at 80°C over a 5-min. period.

Next, it was thermally treated at 140°C over a 3-min. period, and after it had been /5
washed with water, the deodorizing fabric (E) was obtained.

For comparative purposes, a liquid mixture of a case where a water repellent agent alone was used together [with a deodorizer] was prepared by solubilizing 12.5 g of a deodorizer ("Fresh Shiraimatsu," manufactured by Shiraimatsu Shin'yaku Co.) and 15 g of a cellulose-reactive water repellent agent ("Palladium RC," manufactured by Ohara Palladium Chemical Co.) into 500 mL of water.

After a cotton fabric had been immersed in the aforementioned liquid mixture, it was wrung by using a mangle and then dried.

Next, it was thermally treated at 140°C over a 3-min. period and then washed with water, as a result of which the comparative fabric (F) was obtained.

For comparative purposes, furthermore, a liquid mixture of a case where a resin alone was used together [with the deodorizer] was prepared by solubilizing 12.5 g of a deodorizer ("Fresh Shiraimatsu," manufactured by Shiraimatsu Shin'yaku Co.), 30 g of a melamine resin ("Sumitex Resin M-3," manufactured by Sumitomo Chemical Co.), and 4 g of an organic amine salt-type catalyst ("Catalyst 376," manufactured by Dai-Nihon Ink Chemical Co.) into 500 mL of water.

After a cotton fabric had been immersed in the aforementioned liquid mixture, it was wrung at 100% by using a mangle and then dried.

Next, it was thermally treated at 140°C over a 3-min. period and then washed with water, as a result of which the comparative fabric (G) was obtained.

The respective deodorizing efficiencies of the deodorizing fabric (E), (F), and (G) thus obtained before and after the wash cycles are shown below.

Table III: Hydrogen sulfide deodorizing efficiency

(hydrogen sulfide concentration: 80 ppm)

Deodorizing fabric	Deodorizing efficiency (%)		
	Pre-wash	10 wash cycles	30 wash cycles
E (Present invention)	75	45	40
F (comparative example)	75	0	0
G (comparative example)	0	0	0
Blank	0	0	0

[Note: "Monogen" (manufactured by Dai-Ichi Kogyo Co.) was used as a detergent]

Application Example 4

A liquid mixture was prepared by diluting 5 g of a deodorizer which included a flavonic compound ("Pansil," manufactured by Release Science Co.), 15 g of a cellulose-reactive water repellent agent ("Palladium AV," manufactured by Ohara Palladium Chemical Co.), 30 g of a melamine resin ("Sumitex Resin M-10," manufactured by Sumitomo Chemical Co.), and 4 g of zinc borofluoride with 500 mL of water.

After a polyester/cotton mix-spun fabric had been immersed in the aforementioned liquid mixture, it was wrung at 80% by using a mangle and then dried.

Next, it was thermally treated at 140°C over a 3-min. period and then washed with water, as a result of which the deodorizing fabric (G) [sic: Overlap] was obtained.

For comparative purposes, a polyester/cotton mix-spun fabric was treated with a liquid mixture obtained by diluting 2.5 g of the Pansil deodorizer with 500 mL of water, as a result of which comparative fabric (H) was obtained.

The respective deodorizing efficiencies of the deodorizing fabric (G) and (H) thus obtained before and after the wash cycles are shown below.

Table IV: Ammonia deodorizing efficiency

(ammonia concentration: 200 ppm)

Deodorizing fabric	Deodorizing efficiency (%)		
	Pre-wash	10 wash cycles	30 wash cycles
G (Present invention)	80	50	45
H (comparative example)	80	0	0
Blank	0	0	0

[Note: "New Beads" (manufactured by Kao Co.) was used as a detergent]

Application Example 5

A liquid mixture was obtained by solubilizing 5 g of a deodorizer which included a flavonic compound ("Asutenchi P-110," manufactured by Yamato Chemical Co.), 15 g of a cellulose-reactive water repellent agent ("Palladium RC," manufactured by Ohara Palladium Chemical Co.), 30 g of a melamine resin ("Sumitex Resin M-3," manufactured by Sumitomo Chemical Co.), and 2 g of an organic amine salt-type catalyst ("Catalyst 376," manufactured by Dai-Nihon Ink Chemical Co.) into 500 mL of water.

After a cotton fabric had been immersed in the aforementioned liquid mixture, it was wrung at 100% by using a mangle and then dried.

Next, it was thermally treated at 140°C over a 3-min. period and then washed with water, as a result of which the comparative fabric (I) was obtained.

For comparative purposes, a cotton fabric was treated with a liquid mixture obtained by diluting 5 g of the aforementioned deodorizer Asutenchi P-110 with 500 mL of water, as a result of which comparative fabric (J) was obtained.

The respective deodorizing efficiencies of the deodorizing fabric (I) and (J) thus obtained before and after the wash cycles are shown below.

Table V: Ammonia deodorizing efficiency

/6

(ammonia concentration: 150 ppm)

Deodorizing fabric	Deodorizing efficiency (%)		
	Pre-wash	10 wash cycles	30 wash cycles
I (Present invention)	80	55	45
J (comparative example)	80	0	0
Blank	0	0	0

[Note: "Monogen" (manufactured by Dai-Ichi Kogyo Seiyaku Co.) was used as a detergent]

Application Example 6

A liquid mixture was prepared by solubilizing 5 g of a deodorizer which included a flavonic compound extracted from a Theaceae plant (manufactured by Shiraimatsu Shin'yaku Co.), 15 g of a cellulose-reactive water repellent agent ("Palladium RC," manufactured by Ohara Palladium Chemical Co.), and 30 g of an epoxy resin ("Denacol EX 810," manufactured by Nagase Sangyo Co.) into 500 mL of water.

After a cotton fabric had been immersed in the aforementioned liquid mixture, it was wrung at 100% by using a mangle and then dried at 80°C over a 5-min. period.

Next, it was thermally treated at 140°C over a 3-min. period and then washed with water, as a result of which the comparative fabric (K) was obtained.

For comparative purposes, a cotton fabric was treated with a liquid mixture obtained by diluting 5 g of the aforementioned deodorizer with 500 mL of water, as a result of which comparative fabric (L) was obtained.

The respective deodorizing efficiencies of the deodorizing fabric (K) and (L) thus obtained before and after the wash cycles are shown below.

Table VI: Hydrogen sulfide deodorizing efficiency

(hydrogen sulfide concentration: 80 ppm)

Deodorizing fabric	Deodorizing efficiency (%)		
	Pre-wash	10 wash cycles	30 wash cycles
K (Present invention)	75	50	40
L (comparative example)	75	0	0
Blank	0	0	0

[Note: "Monogen" (manufactured by Dai-Ichi Kogyo Co.) was used as a detergent]

(Results)

As has been discussed in detail above, the method wherein a fiber product is treated with a liquid mixture of a deodorizing composition which includes, as an effective component, a flavonic compound, a terpenic compound, or a porphyrin-metal complex compound together with a cellulose-reactive water repellent agent and a resin processing agent can be easily implemented by using extant resin processing apparatuses for fiber products.

Since the wash resistance of the product is excellent, furthermore, it may be applied to diverse applications such as garments, bedroom accouterments, etc.

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